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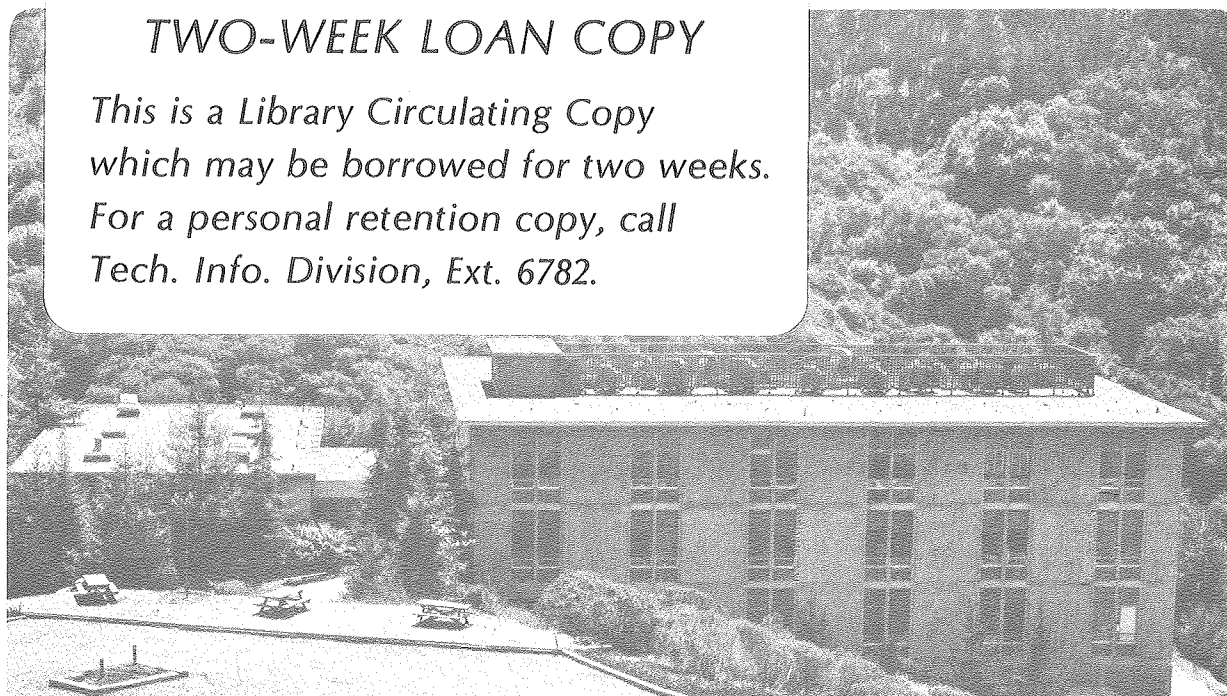
Hydrolytic Polymerization of Chromium (III).

II.   A Trimeric Species

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Abstract

Using an ion-exchange displacement elution, a green species was separated from mixtures of $Cr(III)$ polymers and its absorption spectrum determined. The hydroxides per chromium atom were found to be 4/3 and the charge per chromium atom was shown to be consistent with this value. The degree of polymerization from freezing point depression was close to 3. Measurements are reported for the equilibrium quotient for the formation of the trimer from the monomer. The ESR spectrum and magnetic susceptibility were determined, and the results are discussed in terms of possible structures.

Laswick and Plane (2) reported the isolation of a green polymeric species

(2) J.A. Laswick and R.A. Plane, J. Am. Chem. Soc., 81, 3564 (1959)

from refluxed solutions of chromium (III) perchlorate by ion exchange techniques, using a 0.2M solution of $La(ClO_4)_3$ as eluant. Their investigation showed the green species to be a more highly polymerized form than a second species, later identified as a dimer (3,4,5), also isolated from the same refluxed solutions. Their conclusion was based upon the observed elution behavior: the green species

(3) M. Ardon and A. Linenberg, J. Phys. Chem., 65, 1443 (1961)

(4) R.W. Kolaczkowski and R.A. Plane, Inorg. Chem., 3, 322 (1964).

(5) M.E. Thompson and R.E. Connick, Inorg. Chem., 20, xxx (1981); hereafter referred to as Paper I.

is more tightly held than the dimeric species and is far more sensitive to eluant concentration. A spectrum of the green polynuclear species was also reported.

Sannikov, Krylov and Vinogradov (6) have reported spectrophotometric evidence

(6) Yu. I. Sannikov, E.I. Krylov and V.M. Vinogradov, Russian Journal of Inorganic Chemistry, 12, 1398 (1967) English translation.

for the doubly bridged dimer, two tetramers, ($Cr_4(OH)_4^{8+}$ and $Cr_4(OH)_6^{4+}$) but no trimer. Since the identification depended on curve resolution of the spectra of equilibrium mixtures -- a hazardous undertaking considering the similarity in spectra of Cr(III) species (see Fig. 1 of Paper 1) -- the conclusions are open

to question. The equilibrium amounts of doubly bridged dimer reported are more than an order of magnitude higher than estimated from the results of Paper 1.

In the present work the green species was isolated in solution as the perchlorate salt except for the presence of a small amount of perchloric acid. Such pure samples were then used to establish the number of hydroxide (or oxide) ions per chromium by two methods. The degree of polymerization was determined from the freezing point depression of the perchloric acid eutectic and confirmed with equilibrium measurements for the formation from the monomer. The pure solutions were used to measure the following properties of the trimer: absorption spectrum, magnetic susceptibility and electron spin resonance.

Experimental. Chromium (III) solutions containing the green species as well as other polymers and the monomer were prepared either by reflexing $Cr(NO_3)_3$ solutions or by dissolving metallic chromium in perchloric acid to give a high concentration of chromous ion which was then oxidized to Cr(III) by bubbling oxygen through the solution (7). The latter method gave a better yield of the green species and higher polymers.

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(7) M. Ardon and R.A. Plane, J. Am. Chem. Soc., 81, 3197 (1959).

Isolation of the green polynuclear species was carried out (8,9) by a displacement development from ion exchange column using thorium (IV) perchlorate as

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(8) J.E. Finholt, UCRL-8879, April 16, 1960, Lawrence Radiation Laboratory Report; thesis, University of California, Berkeley, April 16, 1960.

(9) G. Thompson, UCRL-11410, Lawrence Radiation Laboratory Report, Berkeley, CA, June 1964; thesis, University of California, Berkeley, June 1964.

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the displacing agent. Two different types of resin proved successful in this type of separation; a colloidal form of Dowex 50W-X12 (no longer available) and Dowex 50W-X2 or X4, 200-400 mesh, both in the hydrogen ion form. Use of this method allowed the separation and collection of pure, concentrated samples of individual chromium(III) species uncontaminated by any cationic species other than hydrogen ion -- a distinct advantage over simple elution separation.

Isolated, pure fractions of the green species were used to determine the number of hydroxide groups per chromium atom by the following method. After the solution was analyzed for concentration of free hydrogen ion and for chromium, it was made alkaline by adding a known amount of sodium hydroxide and oxidized by heating with an excess of 30 percent hydrogen peroxide. The alkali content was then determined by a potentiometric titration with standardized HCl solution to an endpoint of about pH 4.2. The number of hydroxide groups per chromium atom can be calculated from the following expression:

$$OH^-/Cr = \frac{4C + H_1 + H_2 - B}{C}$$

where C is the number of gram-atoms of chromium, B the equivalents of base added, H_1 the equivalents of acid used in the titration, and H_2 the equivalents of free hydrogen ion present initially. The equation for the oxidation of the polymer is given by:

$$\frac{2}{x} Cr_x(OH)_y^{3x-y} + 3H_2O_2 + (8 - \frac{2y}{x}) OH^- = Cr_2O_7^{2-} + 7H_2O$$
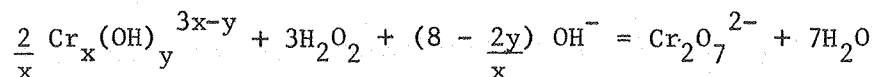
Freezing point lowering experiments were made with fresh samples of the green species prepared from refluxed chromium(III) perchlorate solutions using Dowex 50W-X2. The procedure for measurement is described in Paper I.

The equilibrium measurements were made as described for the dimer in Paper I, and, in fact, the same solutions were usually analyzed for both dimer and trimer. The trimer was the last species eluted. Some additional chromium(III) species were not eluted from the column by the $Ca(ClO_4)_2$ solution and are presumed to be higher polymers.

Magnetic susceptibility and ESR measurements were made as described in Paper I. Pure solutions of trimer were prepared from a refluxed solution of 1.0M Cr(III) perchlorate of $\sim$ pH 3.5 with Dowex 50W-X4, 200-400 mesh, and displacement by 0.25M thorium perchlorate.

Results and Discussion

Absorption Spectrum. The visible and ultraviolet absorption spectrum of the green species is shown in Fig. 1 of Paper I as that of $Cr_3(OH)_4^{5+}$. The general appearance is the same as reported by Laswick and Plane (2), but the absorbance per mole chromium(iii) is uniformly lower in the present results by about 7 percent. The striking similarity of the spectra of all chromium species of Fig. 1 of Paper I indicates little change in structure and probably argues for H_2O or bent OH^- bridges as coordinating ligands in all cases.

Hydroxides Per Chromium Atom. The experimental results for the determination of the hydroxides per chromium atom of the green polymer, i.e. y/x in the formula $Cr_x(OH)_y^{3x-y}$, are presented in Table 1. Columns 2,3,4 and 5 correspond to C, H_2, H_1, and B, respectively of the Experimental section. The uncertainty is an estimate of the experimental accuracy. The data lead to an average value of 1.35 which is close to 4/3. The result would be consistent with a trimer containing four hydroxide groups or a multiple of this composition.

Charge Per Chromium Atom. Two methods were tried. In method 1 the procedure of Connick and Cady (10) was used in which the concentration of chromium

(10) H.W. Cady and R.E. Connick, J. Am. Chem. Soc., 79, 4242 (1957); 80, 2646 (1958).

Table 1. Hydroxide ions per chromium atom for the green species

Sample source	mg atoms of Cr	Initial meq free H^+	Added meq OH^-	meq H^+ used in titration	OH^-/Cr atom
Hydrolyzed $Cr(ClO_4)_3$	0.487	0.157	2.00	0.567	$1.38 \pm .05$
Hydrolyzed $Cr(NO_3)_3$	0.144	0.070	1.008	0.550	$1.31 \pm .05$

in gram atoms per liter was measured for the green solution as it came off the column in its preparation by displacement elution. The anion concentration of this solution, assumed to be the same as that of the displacement solution of $Th(ClO_4)_4$, was determined by running the displacement solution into a column in the hydrogen ion form and titrating aliquots of the eluted solution for hydrogen ion. The free hydrogen ion concentration in the green species solution was determined by pH measurement. The results can be expressed as

$$\text{Charge per chromium atom} = \frac{a - [H^+]}{[Cr]}$$

where a is the total anion charge concentration in the eluted green solution in equivalents per liter, $[H^+]$ is the free hydrogen in concentration, and $[Cr]$ is the chromium concentration in gram atoms per liter.

In Method 2 an aliquot of the pure green solution was added to a column of resin in the hydrogen ion form, and the hydrogen ions displaced were washed out with water and titrated to give the equivalents of charge per liter in the aliquot. The chromium concentration in gram atoms per liter and the free hydrogen ion concentration were determined as before. The same formula as for Method 1 applies. Results are shown in Table 2.

Method 1 yields lower results for the charge per Cr atom than Method 2. The second method was tried because of evidence (8) that the green species associates some perchlorate ion with it in the resin. In Method 2 any such loosely bound ClO_4^- would be washed out by the water, thus yielding the charge per chromium resulting from the chromium and hydroxide ions only in the species. The average value of 1.73 positive charges per chromium is reasonably consistent

Table 2. Charge per chromium atom of the green species

Sample	Method	Total charge concentration (equiv/1)	pH	$[H^+]$ M	[Cr] (g atom/1)	Charge per Cr atom
1	1	1.100	1.72[a]	0.194	0.599	1.51 ± .04
2	1	1.100	1.72[a]	0.194	0.591	1.53 ± .04
3	1	1.100	1.72[a]	0.194	0.607	1.49 ± .04
2	2	1.211	1.72[a]	0.194	0.591	1.72 ± .04
3	2	0.1274	1.72	0.0197	0.0617	1.74 ± .04

[a] pH is of the sample diluted 1.016 cc to 10.00 cc.

with the hydroxides per chromium results determined earlier. For the formula

$Cr_x(OH)_y^{+3x-y}$ a value of y/x = 4/3 yields 5/3 = 1.67 for (3x-y)/x, the charge

per chromium atom. If consideration is restricted to a trimer, the Method 2

results are consistent only with a charge per chromium atom of 5/3.

In this and the previous determination of the formula, no distinction can

be made between oxide ions and twice as many hydroxide ions. Hydroxide ions

have been used for simplicity in expressing the results and because the spectrum

and considerations of acidity constants make it likely that only hydroxide ions

are involved.

While a comparison of the results of Methods 1 and 2 gives strong evidence

for the association of perchlorate ion with the green polymer in the resin,

these results give no information about such a possible association in the

aqueous solution.

Attempts (8) to determine the charge per species by the method of Connick

and Cady (10) yielded a value of only ca. 3.6 instead of a multiple of 5, pre-

sumably because of perchlorate ion association with the green species in the

resin, although activity coefficient problems may have been greater than expected.

Degree of Polymerization from Freezing Point Lowering.

Since the charge per species determination by ion exchange failed, the

degree of polymerization was investigated directly by the lowering of the

freezing point of a eutectic mixture of water and perchloric acid on the

addition of the green species (11, 12, 3). Since the solution of the green

(11) P. Souchay, Bull. Soc. Chim. France, 15, 143 (1948).

(12) H.J. Muller, Annales de Chimie [11] 8, 143 (1937).

species contained only perchlorate anions, a little hydrogen ion, water and the green species, the freezing point lowering responds only to the added foreign species, i.e. the green polymer. Ardon and Linenberg (3) report the molar freezing point constant for a number of metal perchlorates to be $K_f = 4.43$ degrees per mole per kilogram of eutectic mixture, with an uncertainty of 7 percent.

The results are given in Table 3 where it is seen that the value of $mK_f/\Delta T$, which corresponds to the number of chromium atoms per green species, is 3; therefore the polymer is a trimer. From the earlier results it contains 4 hydroxides and is $Cr_3(OH)_4^{5+}$. From here on we will refer to it as the trimer, rather than the green species.

Table 3. Cryoscopy of the Trinuclear Species

Moles Cr(III) added per kg eutectic mixture	ΔT	$\dfrac{mK_f^{\dagger}}{\Delta T}$
0.00616	0.0090°	3.03
0.0124	0.0184	2.99
0.0284	0.0423	2.97
0.0455	0.0670	3.01

$\dagger$ m is moles Cr(III) per kilogram 40.7% perchloric acid.

Equilibrium Measurements. Values of the equilibrium quotient for the formation of the trimer from the monomer are of importance in assessing its stability and understanding its role in the chemistry of Cr(III). To calculate the quotient, the following equilibrium was used:

$$3Cr^{+3} + 4H_2O \xrightarrow{Q_{34}} Cr_3(OH)_4^{+5} + 4H^+,$$
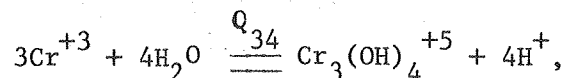
where $Q_{34} = \dfrac{[Cr_3(OH)_4^{+5}] \; [H^+]^4}{[Cr^{+3}]^3}$.

Correction for the formation of $CrOH^{+2}$ according to the equation:

$$Cr^{+3} + H_2O \xrightarrow{ Q_{11} } CrOH^{+2} + H^+$$

(13)
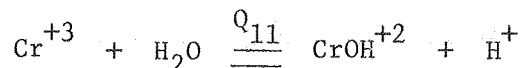
was made using values for Q_{11} obtained from Postmus and King's hydrolysis

measurements of chromium(III) perchlorate solutions at an ionic strength of

0.034 M and corrected to the desired ionic strength using ionic strength de-

pendence data for the first hydrolysis of Fe^{3+} in sodium perchlorate solutions

at 25°C (14).

(13)   C. Postmus and E.L. King, J. Phys. Chem., 59, 1208 (1955)

(14)   L. G. Sillen and A. E. Martell, Stability Constants of Metal-Ion Complexes,

The Chemical Society, Special Publication No. 17, 1964.

The experimental results are given in Table 4. At constant ionic strength,

there is no systematic variation in Q_{34} as the initial chromium and the hydrogen

ion concentrations were varied as much as a factor of 4, although the constancy

of Q_{34} leaves much to be desired. This irreproducibility arises in part from

the high powers of hydrogen ion and chromic ion concentrations entering into

the calculation, as well as from the irreproducibility of the analysis for Cr^{3+}

and trimer by the ion-exchange separation. An error of 0.04 pH units changes

Q_{34} by nearly a factor of 1.5.

The predicted Debye-Hückel limiting law ionic strength dependence is a slope

of 1.07 for log Q_{34} versus $\sqrt{\mu}$ at 50°. The data are in qualitative agreement with this

prediction and show an increasing value of Q_{34} up to an ionic strength of 2 M

Table 4. Equilibrium Quotient for the Formation of $Cr_3(OH)_4^{5+}$

μ M	$[H^+]$ $Mx10^3$	$[Cr^{3+}]_o^{**}$ $Mx10^2$	$[Cr(H_2O)_6^{3+}]$ $Mx10^2$	$[Cr_3(OH)_4^{5+}]$ $Mx10^3$	Q_{34} $x10^8$	
			67.5° C			
0.201	4.5	2.94	1.32	1.94*	35*	
1.00	5.7	2.50	1.32	1.93	89	⎫
1.00	6.5	10.0	2.97	7.7	53	⎪
1.00	6.6	2.50	1.48	1.85	108	⎬ Ave. 76
1.00	25.0	10.4	8.4	0.82*	54*	⎭
2.00	18.5	20.0	13.1	16.1	84	
2.00	20.9	29.5	14.7	27.7	167	
			50.0° C			
0.184	3.78	2.50	1.61	1.06*	5.2*	
0.74	7.4	10.0	6.7	4.30*	4.3*	
1.00	7.6	10.0	6.4	6.6	8.4	⎫
1.00	7.7	2.60	2.29	0.173	5.1	⎪
1.00	9.1	2.60	2.38	0.192	9.8	⎬ Ave. 14, omitting next to last expt.
1.00	9.9	10.0	5.7	5.5	29.	⎪
1.00	11.5	10.4	8.6	3.32	9.1	⎪
1.00	12.0	10.4	9.2	1.21	3.2	⎪
1.00	15.1	10.4	8.9	2.76	20.	⎭
			37.5° C			
0.185	2.35	2.50	1.59	1.30	0.99	
0.74	6.7	10.4	7.3	5.6	2.9	
1.00	2.62	2.50	1.44	1.64	2.6	⎫
1.00	5.9	10.0	6.6	8.0	3.4	⎬ Ave. 2.9
1.00	5.9	10.0	6.3	5.8	2.8	⎭

* Some of the green trimer may not have been removed from the column in the analysis and therefore these values may be somewhat low.

** Total chromium concentration in the equilibrated solution.

with a slope probably somewhat less than the limiting law value, as is usually the case.

From average values of Q_{34} at ionic strength unity in Table 4 one estimates ΔH to be approximately 23 kcal and ΔS at 25° C to be about 75 e.u.. The entropy increase may result from the following factors: (1) there are eight fewer water molecules ordered in the primary coordination sphere of the three metal ions, (2) the concentration of positive charge of the 3 chromic ions has been partly compensated for by the dispersal of 4 positive hydrogen ions, and (3) the +5 charge of the trimer is spread over a large volume and therefore is not nearly as effective as that of a monatomic ion in ordering solvent water.

Magnetic Susceptibility and ESR Measurements.

The magnetic susceptibility gives information on the intensity of magnetic interaction between neighboring chromium atoms in the polymer, and therefore potentially contains structural and bonding information. Results for the trimer are shown in Table 5 along with the effective magnetic moment in Bohr magnetons. Values of χ_A were calculated from experimental data as described in Paper I.

Table 5. Magnetic Susceptibility

T(°C)	$X_A \times 10^6$	μ_{eff} (B.M.)
274.0	4,920	3.29
290.2	4,681	3.30
300.0	4,543	3.30
308.7	4,425	3.31
318.4	4,309	3.31
329.9	4,158	3.30

Although the magnetic properties of several dimeric complexes of chromium(III), bridged by either oxide or hydroxide groups, have been investigated (15,16,17), only one trimeric species has been extensively studied: $[Cr_3O(CH_3CO_2)_6(H_2O)_3]^+$.

(15) A. Earnshaw and J. Lewis, J. Chem. Soc., 1961, 396

(16) D.J. Hodgson, Prog. Inorg. Chem., 19, 173 (1975) and references quoted therein.

(17) J. Josephson and E. Pedersen, Inorg. Chem., 16, 2534 (1977)

It is best described as an equilateral triangle of chromium(III) atoms surrounding an O^{2-} and with O-C-O links between the Cr atoms. (18) The J/k value reported is $-10.4°$ and μ_{eff} at room temperature in solution is 3.37 B.M. (19) A further

(18) B.N. Figgis and G.B. Robertson, Nature, 205, 694 (1965)

(19) A. Earnshaw, B.N. Figgis, and J. Lewis, J. Chem. Soc. A, 1966, 1656

example of a chromium(III) complex whose magnetic properties have been examined is $[Cr_4(OH)_6(en)_6]^{+6}$, a planar rhomboid of chromium atoms held together by four

bridging hydroxo groups and with two of the opposing chromiums bridged by an
additional pair of hydroxides (20,21). The two values of J/k equal to -10
and -20.5° correspond to coupling in the rhomboid and between the chromiums
bridged by the additional pair of hydroxides, respectively.

(20) M.T. Flood, R.E. Marsh, and H.B. Gray, J. Am. Chem. Soc., 91, 193 (1969)

(21) M.T. Flood, C.G. Barraclough, and H.B. Gray, Inorg. Chem., 8, 1855 (1969)

In the complex reported here, the bridging groups were assumed to be hydroxide
groups since their presence has been established for both of the dimeric species (5).
Two different arrangements of chromium(III) atoms have been postulated for trimeric
species: an equilateral triangle with the chromium atoms at the vertices or a
linear array of chromium atoms. (See Figure 1a and 1b.) For the first structure,
the Hamiltonian, following Kambe's general procedure (22), as all other treat-
ments whose J values are reported do, is given by:

$$H_j = -2(J_{12}\underline{S}_1 \cdot \underline{S}_2 + J_{23}\underline{S}_2 \cdot \underline{S}_3 + J_{31}\underline{S}_1 \cdot \underline{S}_3)$$

where the J_{ij}'s and the S_i's are equal since the atoms composing the system are

(22) K. Kambe, J. Phys. Soc. Japan, 5, 48 (1958)

equivalent. The energy levels are $-J[S'(S' + 1)-3S(S + 1)]$ where S' is the
total spin and S the spin of one chromium, i.e. 3/2. The expression for the
variation of atomic susceptibility with temperature is then given by:

$$\chi_A = \frac{g^2N\beta^2}{12kT} \left\{ \frac{2 + 40\exp(-3x) + 105\exp(-8x) + 168\exp(-15x) + 165\exp(-24x)}{2 + 8\exp(-3x) + 9\exp(-8x) + 8\exp(-15x) + 5\exp(-24x)} \right\} + N(\alpha)$$

where $x = -J/kT$, g is the spectroscopic splitting factor, and $N(\alpha)$ is the temperature-independent, high-field paramagnetic factor. For the second structure (Figure 2b), if it assumed that the exchange integral between the central and end chromium atoms is the same for either end of the complex and the exchange integral between the end chromiums is zero, the energy states become:

$$-J \left\{ \underline{S}'(\underline{S}' + 1) - \underline{S}(\underline{S} + 1) - \underline{S}*(\underline{S}* + 1) \right\}, \text{ where } \underline{S}* = \underline{S}_1 + \underline{S}_3 = 3,2,1,0$$

and $\underline{S}' = \underline{S}_1 + \underline{S}_2 + \underline{S}_3 = 9/2, 7/2, 5/2, 3/2, 1/2$, and the central chromium is numbered 2. The magnetic susceptibility is given by:

$$\chi_A = \frac{g^2N\beta^2}{12kT} \left\{ 165\exp(-21x) + 84[\exp(-12x) + \exp(-18x)] + 35[\exp(-5x) + \exp(-11x) + \exp(-15x)] \right.$$
$$+ 10[1 + \exp(-6x) + \exp(-10x) + \exp(-12x)] + \exp(-7x) + \exp(-3x) \left\} \middle/ \left\{ 5\exp(-21x) \right.$$
$$+ 4[\exp(-12x) + \exp(-18x)] + 3[\exp(-5x) + \exp(-11x) + \exp(-15x)]$$
$$+ 2[1 + \exp(-6x) + \exp(-10x) + \exp(-12x)] + \exp(-7x) + \exp(-3x)] \right\} + N(\alpha)$$

Independent measurements of the g value (= 1.942) of the trimer were carried out by ESR (Paper 1, Fig. 3 (d)), and thus J and $N(\alpha)$ are the only parameters to be fitted. In the fitting $N(\alpha)$ was assumed to be zero because it is generally small for Cr(III) (15) and has a minor effect on the fitting. The experimental $1/\chi_A$ values, plotted in Paper 2, Fig. 4 as a function of temperature, lie on a good straight line. The slope of this line, however, is appreciably greater than the theoretical line calculated from either the symmetric triangle model

or the linear model by about 19 percent in both cases. The reason for this discrepancy is not apparent. If the theoretical curves are made to pass through about the middle temperature of the data, values of J/k of −16° and −22° are found for the symmetric triangle and the linear models respectively. The fit does not help to distinguish between the two structures (23).

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(23) In reference (9), because of a calculational error, it was erroneously concluded that the linear model was preferred.

Because of the similarity (24) of the spectrum to that of $Cr(H_2O)_6^{3+}$ (Paper I, Fig. 1) and the relatively small value of −J/k (25) it is likely that the chromiums are not connected by linear oxide bridges, but rather by bent oxide or hydroxide bridges. (15) From the empirical formula, acidity considerations, and symmetry of structures, it is likely that only OH^- groups would be present in the two structures of Fig. 1. The value of −J/k = 22° for the linear structure seems rather large compared to values of 6° to 10° in double hydroxide bridged dimers (except for the tetramer (20,21)). It is more difficult to predict a −J/k value for the symmetric triangular structure of Fig. 2a, but the experimental value of 16° would appear possible.
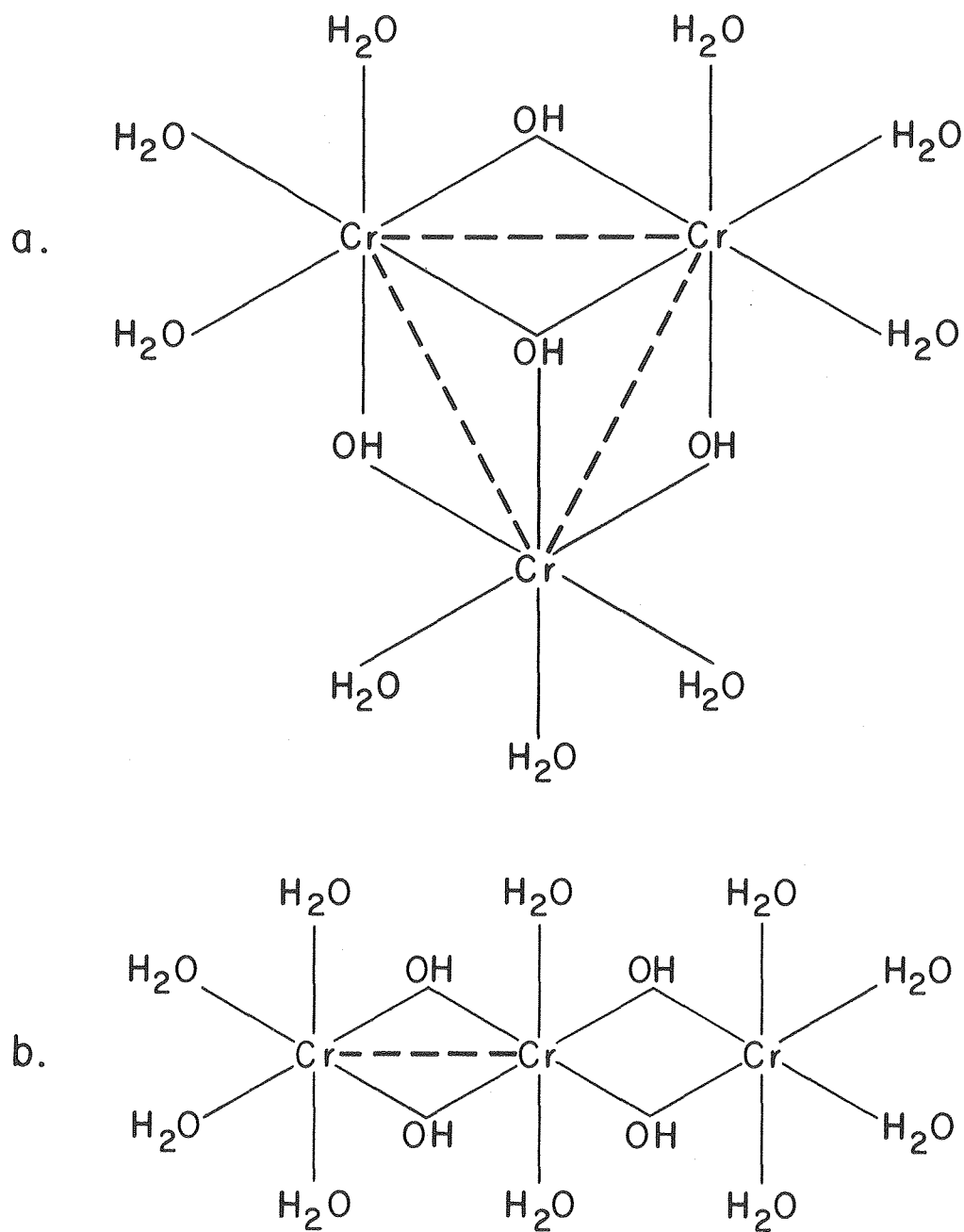
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(24) C.E. Schäffer, J. Inorg. Nucl. Chem., 8, 149 (1958)

(25) W.K. Wilmarth, H. Graff and J.T. Gustin, J. Am. Chem. Soc., 78, 2683 (1956)

ACKNOWLEDGMENT

Fig. 1. Possible structures of the chromium(III) trimer: (a) the symmetric triangular structure, (b) the linear structure.

Figure 1